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(71) Applicant Owens-Illinois, Inc., Post Office Box 1035, Toledo, State of Ohio 43666, United States of America
(72) Inventors Charles Frederick Rapp, Norman Lee Boling
(74) Agent W. P. Thompson & Co.

(54) **Solar Cells and Collector Structures Therefor**

(57) The collector and concentrator comprises a thin luminescent layer 14 on a transparent support 12 and has a small surface area for coupling to a photovoltaic solar cell 18 which receives a major part of the luminescence by internal reflection within the collector. The refractive indices of layers 12, 14 should be close or equal and the thickness ratio of the layers is at least 4:1. The layers may be glass doped with uranyl, chromium or manganese ions, or a polysiloxane or polymethacrylate, and have silvered side surfaces. The layer 14 may contain two luminescent species operating in cascade or the layer 12 may be luminescent and operate in cascade. A silicon cell 18 is coupled by an anti-reflective coating and a layer of oil.

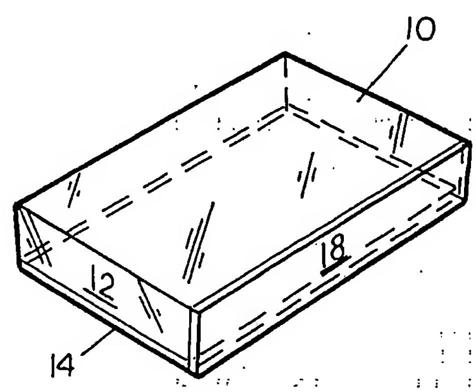

FIG. 6

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FIG. 1

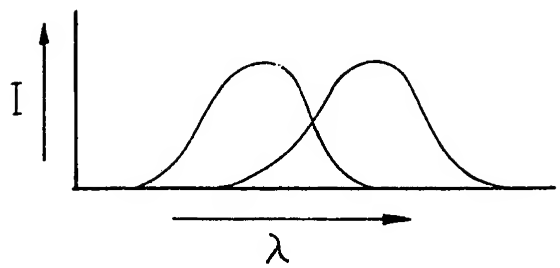


FIG. 2

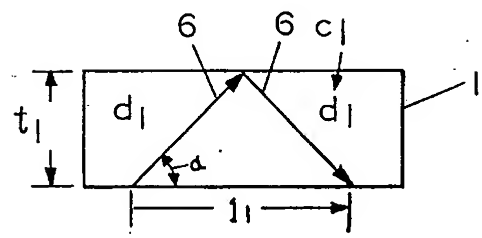


FIG. 3

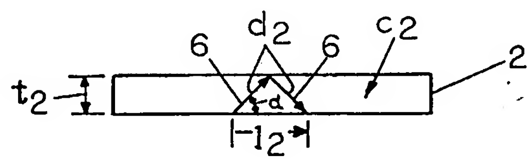
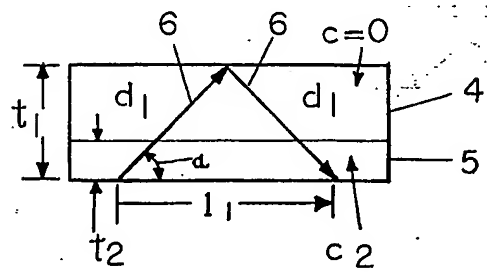


FIG. 4



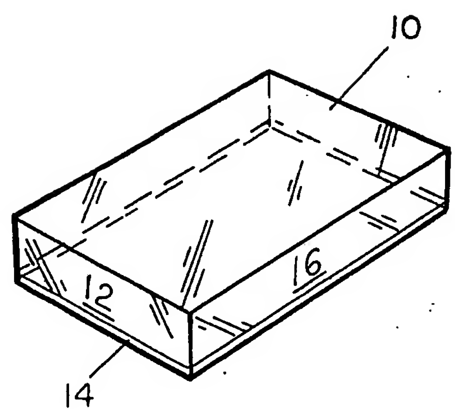


FIG. 5

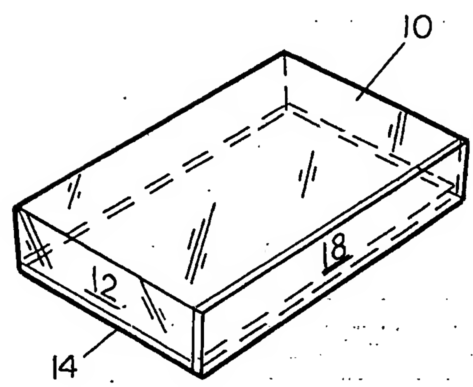


FIG. 6

SPECIFICATION

Solar Cells and Collector Structures Therefor

This invention relates to solar cells using semiconductors to convert sunlight at least a part thereof to electrical energy. Such semiconductors are known as photovoltaic cells or photocells, and common examples of such photocells are silicon or gallium arsenide semiconductors having P-N junctions. Commonly, an electrical lead is connected on either side of the semiconductor across the P-N junction.

Semiconductor photocells are very expensive; in consequence, it has been the practice to form apparatus for converting solar energy so as to gather and concentrate the sunlight reaching a given semiconductor photocell so that such extremely large areas of semiconductor material need not be employed as would be necessary without such a gathering system. The common gathering systems in the past were optical systems, wherein lens systems concentrated the light and focused same on a given photocell.

However, such a lens system was and is relatively expensive and is not useful in diffuse light on a cloudy day.

More recently, however, there has been conceived a different type of collector and concentrator of radiation to be impinged on a semiconductor photocell. For instance, Weber and Lambe in Applied Optics, Vol. 15, pages 2299—2300, October 1976, disclose a system whereby a large area sheet of material, such as a rigid plastic or a glass doped with a luminescent material is exposed to solar radiation. The luminescent medium ideally has a strong absorption for the sun's rays, especially in the visible where the solar spectrum peaks, and it emits electromagnetic radiation of a longer wave length suitable for activating the semiconductor photocell. A large portion of the light emitted from the luminescent species is in effect trapped in the collector with essentially total internal reflection until the light reaches the area where a photocell, such as a silicon photocell, is optically coupled to a small area, for instance an edge, of the collector. In this way, the light from the sun is not only converted to more suitable wave lengths for activation of the photocell but is concentrated since the light received by the large area of the collector escapes only in the small area where the photocell is optically connected to the collector.

Another article, by Levitt and Weber, appears in Applied Optics, Vol. 16, No. 10, pages 2684—2689, October 1977, should be read with the article first mentioned.

Other publications aiding in the understanding of the setting of the present invention include Goetzberger, Applied Physics, 14, 123—139, 1977, German Patent Application 2620115 published November 10, 1977 and German Patent Application 2554226 published June 8, 1977, which is of some peripheral interest.

Also, numerous patents deal with the conversion of solar energy to different wave lengths by means of luminescent or fluorescent layers and impinging emitted light on a photocell; examples are U.S. Patents 3,426,212 and 3,484,606, which patents, however, do not have the concept of concentrating the light from a large area and collecting it over a much smaller area by optical coupling to a relatively small area semiconductor photocell.

In the recent prior art structure of the type disclosed in the aforesaid Weber and Lambe publication, which describes what is there termed a "luminescent greenhouse collector", the luminescent medium or layer for practical reasons needs to be self-supporting. Therefore, the luminescent layer obviously must be at least one-half millimeter thick if it is as small as, say, 10 centimeters on a side, or it must be much thicker if it is, say, a meter on a side.

It is an object of the present invention to provide a luminescent collector-concentrator of solar energy of increased efficiency.

It is a further object of the invention to provide such a luminescent solar collector-concentrator optically coupled at a small fraction of its surface to a semiconductor photovoltaic cell to function as a solar cell, that is as a device to convert solar energy to electricity.

According to the present invention, a very thin, or at least a relatively very thin luminescent layer is supported in good optical contact on a radiation conducting support layer ("in optical contact" meaning that there is minimum reflection at the interface of the support layer and the luminescent layer) where the support layer is thick enough for its area to be self-supporting. Thus, the support layer is generally at least one-half millimeter thick, usually thicker, and has a thickness ratio to the thin luminescent layer of more than 4:1 and usually very much higher. The refractive index of the luminescent layer should be the same as that of the support layer or, if not, close to the latter and preferably the support layer, less than the latter, in order to minimize reflection at the interface, although for reasons to be discussed later the reverse situation might be tolerated in certain instances.

The invention will now be described, by way of example, with reference to the accompanying drawings, in which:—

Figure 1 is a hypothetical representation of the absorption and emission bands of a given luminescent species of a given concentration in the luminescent host layer;

Figure 2 depicts schematically a side view of a single thick layer containing throughout a luminescing species;

Figure 3 depicts a thinner layer containing throughout the same luminescing species at a higher concentration, while

Figure 4 depicts a composite layer of the invention wherein the luminescing species in the bottom layer has the same concentration as in Figure 3 and wherein the top layer is the support layer.

The principles of the invention can be seen

more clearly by examining these drawings. Many luminescing materials such as fluorescent organic dyes have some overlap between their absorption and emission bands, as is shown in Figure 1. In the type of collector or concentrator used in the present invention much of the energy emitted in the region of overlap would be reabsorbed and lost, as will be understood by those skilled in the art. This effect becomes more severe as the concentration of the dye is increased. For one thing, the wave length region of overlap in the absorption and emission spectra as in Figure 1 would be much greater. Furthermore, since the dye concentration is increased in a thinner film to maintain the same absorption, loss by reabsorption would increase for this reason alone. Thus, referring to Figures 2, 3 and 4, 1 is a thick self-supporting luminescent material of thickness t_1 comprising a solid host containing a luminescent species in concentration c_1; 2 is a much thinner luminescent material of thickness t_2 comprising the same host containing the same luminescent species in concentration c_2. In Figure 4 the luminescent material 5, identical to 2 of Figure 3, is in optical contact with and supported by thicker, self-supporting material 4 of high optical quality which in this instance contains no luminescent species. The numeral 6 in each figure represents a single ray in each figure being totally internally reflected for distance d_1 or d_2, at a given angle α. In order for the above plates to have the same absorption efficiency for the incident solar light, it must be true that $c_1t_1=c_2t_2$ where c_1 and c_2 are the dye concentrations in the plates 1, 2 and 5. Also, since $t_1/t_2=d_1/d_2$, it can easily be seen that the same reabsorption loss will occur in the total internally reflected luminescence when traveling distances l_1, l_2 and l_1 transversely across the plates of Figures 2, 3 and 4 respectively. Therefore, it can be seen from the above that the same low reabsorption can be accomplished from a very thin layer of host material doped at high concentration, supported on a thick clear plate as can be accomplished from the thick plate at lower concentration. Of course, in Figure 4 there is depicted the idealized situation in which the index of refraction of 4 is the same as that of 5. If the index is somewhat different in the two materials, it will be understood that there will be some change in the angle when the ray in Figure 4 enters 4 or 5 as the case may be, and thus the distance l_1 in Figure 4 will vary somewhat from l_1 in Figure 2, but the principle and advantages of the invention structure still obtain. Moreover, the refractive index, n, of the thin layer should ideally be equal to or less than n of the thick layer, but the reverse is possible if a particular combination of the substrate layer and thin layer with its luminescent species is particularly advantageous in quantum efficiency of light conversion and thus makes it worthwhile to suffer some light loss by reason of the disadvantageous relationship of the indices.

In Figure 5 is depicted a luminescent solar collector of the invention. Figure 6 shows a luminescent solar collector with a semiconductor silicon solar photovoltaic cell covering one edge thereof. Electrical leads are connected to the silicon cell but are not shown. Like parts have the same reference numbers in Figures 5 and 6.

In Figure 5 collector 10 comprises thick self-supporting layer 12 of material capable of conducting electromagnetic radiation and thin layer 14 of plastic, glass, a gel or other suitable host material containing at least one luminescent species capable of absorbing incident solar light and emitting electromagnetic radiation in another wave length, usually a longer wave length. Three edges of the collector are silvered or otherwise coated to reflect light while edge 16 is not. In operation, light from the sun hitting either face of extended area is absorbed in layer 14 and excites the luminescent species which emits radiation of desired wave lengths, as before described with respect to Figure 4.

A large portion of the emitted radiation reflects back and forth by the process of total internal reflection, and reflection from the mirrored edges, until the concentrated light reaches the window of edge 16 where it escapes and is put to use as for instance in Figure 6.

In Figure 6, identical to Figure 5, except that the edge (which is numbered 16 in Figure 5) has semiconductor photovoltaic cell 18, such as a silicon cell having a P-N junction, optically coupled thereto. This can be accomplished for instance by placing an anti-reflective coating on the facing surface of the silicon cell and interposing an oil film of intermediate refractive index (usually about 1.5) between the silicon cell and the edge of the luminescent solar collector or concentrator.

While in connection with the description of Figures 5 and 6, it is explained that three edges have a reflective coating, in its broadest aspect the edges need not be coated with a reflective coating. The concentrator works without such coating, but of course the concentrated light will be emitted through all unmirrored edges. Further, it is possible and in some cases definitely contemplated that the thick supporting layer of my invention such as in Figures 4, 5 and 6 may also have a luminescent species, but it will be understood from the explanation of the basic advantage of my structure as explained in connection with Figures 1—4, that (1) the thick support layer 1 is mainly a radiation conducting layer particularly for radiant energy emitted from the luminescent species in the thin luminescent layer and (2) in its usually preferred embodiment is less absorptive of said radiant energy than said thin layer, but not always. For instance, thick layer 12 of Figures 5 and 6 can contain luminescent species A that absorbs and is activated by wave lengths emitted by luminescent species B in thin layer 14, species A then emitting even longer wave lengths.

Several advantages of the structure of the present invention are apparent on examination. Some of these are as follows:

1. For practical reasons, some form of acrylic resin or plastic, such as poly(methyl methacrylate), was before the present invention the only commercially suitable host for organic luminescent materials. It was the only material that could withstand weather and UV light, had the right transmission properties and was compatible with common fluorescent materials at a low enough price to be practical in an economic sense. In the present invention the thin luminescent layer preferably has a thickness of no more than 0.25 mm, whether or not it contains more than one luminescent species, and therefore layer 14 can be chosen among exotic (expensive) materials to best match the luminescent materials. Thus, it is well-known that the host material can synergistically enhance or shift the properties of the luminescent material, such as a dye, contained therein. For instance, the separation of the peaks of the absorption and emission spectra is influenced by the properties of the solvent, such as the static dielectric constant, for instance.

2. While the thick or supporting layer 12 can still be the fairly inexpensive acrylic resin of high quality, it is a distinct advantage that the support layer can be glass with its high optical quality, extremely low cost and low absorption characteristics. Yet heat sensitive organic luminescent materials can still be used in the collector, but in the thin layer comprising an organic medium such as a plastic.

3. The possibility of using glass as the thick support layer allows it to be doped if desired with an ion such as the uranyl ion or Mn^{II} that absorb in low wave lengths and emit in visible wave lengths that are efficiently absorbed by a suitable dye or chelate that is the luminescent species in the underlying post layer. Or Ce^{III} can be incorporated in the glass, since it absorbs in the UV and thus protects the plastic and the organic luminescent material in the plastic layer from degradation by UV. Moreover, the Ce^{III} is luminescent and emits in the visible spectrum and is thus converted to light that can be used to excite the organic luminescent dye or other luminescent species in the thin plastic layer.

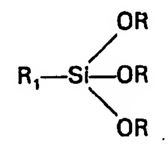
4. A marked advantage is that when two or more luminescent species are used in the thin plastic layer in the manner disclosed in the Swartz *et al.* paper in Optics Letters, Vol. 1, No. 2, August 1977, pp. 73—75, they can be used at a high enough concentration that radiationless (intermolecular) transfer of energy from one luminescent species to the next results. Such raditionless transfer is much more energy efficient. See Th. Forster, Discus, Faraday Soc. 27, 7(1959).

Thus, in one particularly advantageous embodiment of the invention, the thick support layer is glass and the thin layer is a plastic containing a luminescent material. In another, related embodiment, the glass layer contains a UV absorber luminescent material that emits in the visible spectrum.

As luminescent materials useful in the present invention there can be mentioned by way of example fluorescent chelates, fluorescent dyes, inorganic ions and even finely divided solid phosphors, all dispersed in a suitable host as previously discussed.

In a particularly advantageous embodiment the thin layer of the radiation collection medium comprises a thermoset polysiloxane of a trifunctional silane containing the luminescent species dispersed therein.

Such polysiloxane resins can be derived, for instance, by hydrolysis and condensation of silanes of the formula



where R is a lower alkyl radical containing 1—4 carbon atoms, usually methyl or ethyl, and R_1 is an alkyl radical containing 1—6 carbon atoms, an alkenyl radical containing 2—6 carbon atom or is an aryl radical such as phenyl. Mixed condensation products of silanes of the above formula also form suitable polysiloxanes. For further details relative to such polysiloxanes see, for instance, U.S. Patents 3,395,117; 3,388,114 and 3,389,121.

The thermoset polysiloxanes, even though they are relatively expensive, can be economically used as the thin host film or films in the foregoing structure since only a small amount of the resin is required. There are several advantages to such polysiloxanes.

1. They are compatible with most dyes and metallo-organic chelates as well as finely divided inorganic solid phosphors.

2. It has been found that they seal extremely well to glass and most plastics useful as the thick film, such as poly(methyl methacrylate) and they moreover seal to the semiconductor photocell, such as a silicon cell.

3. The index of refraction value of such resins is from about 1.45 to about 1.55, ideal for optical coupling to most glasses and acrylic plastics used for the thick film and for the usual antireflective coating carried on the silicon photocell.

4. They have excellent weathering characteristics, i.e., they are not subject to weathering, i.e., they withstand chemical attack from the atmosphere including water and the usual air pollutants.

5. They are extremely abrasion resistant.

6. They are very resistant to solar ultraviolet light degradation.

7. Very importantly, they can be cured to the thermoset condition at a low enough temperature to avoid harm to even the most heat sensitive of the luminescent organic species, such as dyes and chelates.

Of course, by the term thermoset polysiloxane of a trifunctional silane it is meant to include

polymers derived from trifunctional silanes containing some difunctional or even monofunctional silanes, so long as such polymers are sufficiently cross-linked to be thermoset. Very suitable thermosetting silicon resins are described in U.S. Patent 3,395,117.

In the following examples the dye or chelates was uniformly mixed with a 50 volume percent solution in butyl alcohol of partially cured but further curable polysiloxane resin, prepared as described in Example 1 of U.S. Patent 3,395,117. The coatings on the substrate, in each case clear poly(methyl methacrylate) squares 1/8 inch thick and four inches on a side, were made to achieve a final cured thickness of doped polysiloxane film of about 0.5 mil and of the concentration noted in the respective examples. The solutions were applied to one face of the clean poly(methyl methacrylate) plates and allowed to drain off. The final curing was effected in a drying oven held at 60°C for two days.

Table 1 shows the three test plates, the luminescent species used and its concentration in the thin polysiloxane film coating.

Table 1

Example	Luminescent Species	Concentration, Weight Percent
1 (control)	None	—
2	Rhodamine B	0.15
3	Coumarin 1	0.4

In the tests of the solar concentrators, plus the control, a silicon semiconductor cell having a P-N junction was used. The plates were polished on only one edge and the other edges had no reflective coating. A flat surface of the silicon cell was optically coupled to part of the polished edge. That surface of the cell carried the usual antireflective oxide coating and an index oil of n_D of 1.457 was interposed between the cell and the edge of the luminescent solar concentrator. The silicon cell covered only 8.5 cm of the length of the edge of the luminescent solar concentrator plate in each instance. The same cell was used in each example so that the results are comparable. The cell was connected through electrical leads to tests instruments by which the short circuit current was measured with the sun on a bright day shining on the acrylic surface of the concentrator. The solar cell was shielded from the sun's direct rays. The results in milliamperes is shown in Table 2, together with the brightness of the sunlight as measured by a lightmeter.

Table 2

Example	Illumination (BTU/hr/ft²)	Short Circuit Current (milliamps)
1	300	17.7
2	250	51.9
3	300	23.1

As will be evident to those skilled in the art, various modifications of this invention can be made or followed in the light of the foregoing disclosure and discussion without departing from the scope of the appended claims.

Claims

1. A luminescent solar collector and concentrator cell comprising a radiation collection medium for receiving incident solar radiation, said medium containing at least one luminescent species capable of emitting luminescent radiation upon excitation with incident solar radiation, said medium being totally internally reflective of a major portion of said emitted luminescent radiation, and said medium providing a relatively small surface area for optically coupling to a photovoltaic solar cell responsive to said emitted luminescent radiation, wherein said radiation collection medium is a composite structure comprising a thin layer containing at least one luminescent species, said layer being optically coupled to a thick radiation conducting layer of at least 0.5 mm thickness, which thick layer (1) is totally internally reflective of a major portion of said emitted luminescent radiation, (2) has an index of refraction close to that of said thin layer, and (3) has a thickness ratio to said thin luminescent layer of higher than 4:1.

2. A collector and concentrator, wherein said thick layer also contains a luminescent species.

3. A collector and concentrator according to claim 2, wherein said thin layer contains at least two luminescent species, the first of which has an emission spectrum overlapping the absorption spectrum of the other, said two luminescent species having a concentration sufficiently high that the major mode of activation of said other species by said first species is radiationless.

4. A collector and concentrator according to claim 1, 2 or 3, wherein said thick layer is a glass and said thin layer is a plastics containing said at least one luminescent species.

5. A collector and concentrator according to claim 4, wherein said glass contains a luminescent species which absorbs ultraviolet light and emits light of a longer wave length.

6. A collector and concentrator according to any of the preceding claims, wherein said thick layer is less absorptive of said emitted luminescent material than said thin layer.

7. A solar collector and concentrator substantially as hereinbefore particularly described with reference to the Examples.

8. A solar collector and concentrator substantially as hereinbefore described with reference to the accompanying drawings.

9. A solar cell comprising a solar collector and concentrator according to any of the preceding claims and a photovoltaic cell coupled to said relatively small surface.

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